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<b>(54) Title: AQUEOUS POLYURETHANE DISPERSIONS USEFUL FOR PREPARING POLYMERS WITH IMPROVED MOISTURE RESISTANCE PROPERTIES</b> <b>(54) Titre: DISPERSIONS AQUEUSES DE POLYURETHANNE SERVANT A LA PREPARATION DE POLYMERES A RESISTANCE AMELIOREE A L'HUMIDITE</b>  <b>(57) Abstract</b> <p>The present invention is a polyurethane dispersion that can be used to prepare polyurethane polymers which have moisture resistant properties. Moisture resistant polymers of the present invention are obtained by preparing the polymers from a polyurethane dispersion using a prepolymer formulation which includes an aliphatic mono, di or polyhydroxy compound which has an aliphatic side chain substituent which contains from 5 to 30 carbon atoms.</p> <b>(57) Abrégé</b> <p>Cette invention a trait à une dispersion de polyuréthane pouvant servir à la préparation de polymères à résistance améliorée à l'humidité. On produit ces polymères à partir d'une formulation de prépolymères renfermant un composé aliphatique monohydroxy, dihydroxy ou polyhydroxy pourvu d'un substituant de chaîne latérale aliphatique portant de 5 à 30 atomes de carbone.</p>		

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(54) Title: AQUEOUS POLYURETHANE DISPERSIONS USEFUL FOR PREPARING POLYMERS WITH IMPROVED MOISTURE RESISTANCE PROPERTIES			
(57) Abstract <p>The present invention is a polyurethane dispersion that can be used to prepare polyurethane polymers which have moisture resistant properties. Moisture resistant polymers of the present invention are obtained by preparing the polymers from a polyurethane dispersion using a prepolymer formulation which includes an aliphatic mono, di or polyhydroxy compound which has an aliphatic side chain substituent which contains from 5 to 30 carbon atoms.</p>			

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**Description**

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AQUEOUS POLYURETHANE DISPERSIONS USEFUL FOR PREPARING  
POLYMERS WITH IMPROVED MOISTURE RESISTANCE PROPERTIES

10 This invention relates to polyurethane polymers. This invention particularly  
5 relates to polyurethane polymers obtained from aqueous polyurethane dispersions.

15 Polyurethane dispersions are known, and can be used to obtain polyurethane  
polymers that can themselves be useful in various applications. Polyurethane/urea  
dispersions can be used to obtain, for example: carpet backings; coatings for wood  
finishing; glass fiber sizing; textiles: adhesives; automotive topcoats and primers; films  
20 for packaging; gloves, and other applications. Polyurethane dispersions can be  
prepared by various processes, including, for example, those described in: U.S. Patent  
No. 4,857,565; U.S. Patent No. 4,742,095; U.S. Patent No. 4,879,322; U.S. Patent No.  
3,437,624; U.S. Patent No. 5,037,864; U.S. Patent No. 5,221,710; U.S. Patent No.  
25 4,237,264; and, U.S. Patent No. 4,092,286.

15  
30 Polyurethane dispersions can be obtained according to a process that is  
described in U.S. Application Serial Number 09/039978. Dispersions prepared  
according to the process described therein can be useful for obtaining polyurethane  
carpet backings and polyurethane textile backings. Problems can result, however, in the  
35 20 event that a spill occurs wherein a liquid can flow onto, or be absorbed by, the backing  
on the underside of a carpet. Spilled liquids such as water, urine, beverage drinks, food,  
blood, and feces can penetrate a carpet backing to the underside of the carpet, which  
can be inaccessible to various cleaning methods. Polymeric materials having moisture  
40 resistance can be useful in protective wear such as gloves, for example, or packaging.

25  
45 Various conventional methods can provide a moisture barrier to polymers  
obtained from aqueous polymeric dispersions. For example, increased coating weights  
of a dispersion can be used, thereby increasing the thickness of the polymer.  
50 30 Alternatively, wax added to an aqueous polymeric dispersion can provide a moisture

5 barrier to carpet. Another known method for providing a moisture barrier is to decrease the amount of filler used in a carpet backing formulation. A non-permeable fabric or film can also be applied to a carpet backing, as described in U. S. Pat. No. 5,763,040.

10 Still another method involves applying a fluorochemical on the underside of a  
5 secondary backing, and is described in U.S. Pat. No. 5,348,785. Use of fluorochemicals to impart water impermeability is also described in U.S. Pat. Nos. 4,619,853 and 4,643,930. A water-impervious film is described in U.S. Pat. No. 4,336,089.  
15 Application of various hydrophobic compositions to a secondary backing is described in U.S. Pat. No. 5,558,916.

10  
20 It would be desirable in the art of preparing polyurethane polymers, to prepare a polyurethane dispersion that includes a component that imparts a moisture barrier to a polyurethane polymer, without adding complexity to a manufacturing process, or significantly changing the other properties of the polyurethane polymer. It would also  
25 be desirable in the art to prepare such a polymer by a process that would not significantly increase the cost of manufacture of the polymer, or articles produced therefrom.

30  
35 In one aspect, the present invention is an aqueous polyurethane dispersion comprising an isocyanate terminated prepolymer prepared from a formulation including a polyisocyanate and a polyol mixture, wherein the polyol mixture includes at least one aliphatic mono, di or polyhydroxy compound which has an aliphatic side chain substituent which contains from 5 to 30 carbon atoms and wherein the aliphatic mono, di or polyhydroxy compound which has an aliphatic side chain substituent is present at  
40 25 a concentration of from 0.5 to 10 weight percent of the polymer.

45 In another aspect, the present invention is a moisture resistant polyurethane polymer comprising a polymer layer prepared by applying a layer of an aqueous polyurethane dispersion comprising an isocyanate terminated prepolymer prepared from  
30 a formulation including a polyisocyanate and a polyol mixture, wherein the polyol mixture includes at least one aliphatic mono, di or polyhydroxy compound which has  
50

5 an aliphatic side chain substituent which contains from 5 to 30 carbon atoms and  
wherein the aliphatic mono, di or polyhydroxy compound which has an aliphatic side  
10 chain substituent is present at a concentration of from 0.5 to 10 weight percent of the  
polymer to a substrate and allowing the dispersion to cure.

5  
15 In still another aspect, the present invention is a moisture resistant textile  
comprising a textile and adherent thereto a polymer prepared by applying a layer of an  
aqueous polyurethane dispersion comprising an isocyanate terminated prepolymer  
20 prepared from a formulation including a polyisocyanate and a polyol mixture, wherein  
the polyol mixture includes at least one aliphatic mono, di or polyhydroxy compound  
which has an aliphatic side chain substituent which contains from 5 to 30 carbon atoms  
and wherein the aliphatic mono, di or polyhydroxy compound which has an aliphatic  
25 side chain substituent is present at a concentration of from 0.5 to 10 weight percent of  
the polymer to the textile and allowing the dispersion to cure.

15  
30 Moisture resistant polyurethane of the present invention can be useful in  
cushioned flooring applications such as attached cushion broadloom, carpet tiles, carpet  
underlay, or vinyl flooring; adhesives applications; coatings; protective clothing or  
protective gear such as gloves and aprons; packaging; or any application where  
20 moisture resistant polymers can be useful.

35  
40 In one embodiment, the present invention is an aqueous polyurethane dispersion  
composition that can yield a coating or a foam having good moisture resistance. A  
polyurethane dispersion of the present invention includes water, and either: a  
25 polyurethane; a mixture capable of forming a polyurethane; or a mixture of both. A  
polyurethane dispersion of the present invention can optionally include: chain  
extenders; surfactants; fillers; dispersants; foam stabilizers; thickeners; fire retardants,  
45 and/or other optional materials that can be useful in a polyurethane formulation.

30  
50 The polyisocyanate component of the formulations of the present invention can  
be prepared using any organic polyisocyanates, modified polyisocyanates, isocyanate-

5 based prepolymers, and mixtures thereof. These can include aliphatic and  
cycloaliphatic isocyanates, but aromatic and especially multifunctional aromatic  
isocyanates such as 2,4- and 2,6-toluenediisocyanate and the corresponding isomeric  
10 mixtures; 4,4'-, 2,4'- and 2,2'-diphenyl-methanediisocyanate (MDI) and the  
5 corresponding isomeric mixtures; mixtures of 4,4'-, 2,4'- and 2,2'-  
diphenylmethanediisocyanates and polyphenyl polymethylene polyisocyanates PMDI;  
15 and mixtures of PMDI and toluene diisocyanates are preferred. Most preferably, the  
polyisocyanate used to prepare the prepolymer formulation of the present invention is  
MDI or PMDI.

10 A polyurethane dispersion of the present invention is an aqueous dispersion of a  
polyurethane and/or polyurethane-forming materials. For the purposes of the present  
invention, polyurethane dispersions can include other polymeric and/or oligomeric  
25 compounds including, but not limited to: ureas, biurets, allophanates, and other  
15 compounds having functionality that can be derived from the reaction of an isocyanate  
with the various active hydrogen containing compounds present in the formulation.  
Polyurethane-forming materials, as the term is used in the present invention, are  
30 materials which are capable of forming polyurethane polymers. Polyurethane-forming  
materials include, for example, polyurethane prepolymers. Prepolymers useful in the  
20 practice of the present invention can be prepared by reacting active hydrogen-  
35 containing compounds with an amount of isocyanate in excess of the active hydrogen  
functionality present in the reaction mixture. The isocyanate functionality can be  
present in an amount of from 0.2 wt. percent to 40 wt. percent of the dispersion. A  
40 suitable prepolymer can have a molecular weight in the range of from 100 to 10,000.

25 Prepolymers useful in the practice of the present invention should be  
substantially liquid under the conditions of dispersal. While it is possible to add a  
45 liquid solvent or diluent such as a volatile organic compound (VOC) to the prepolymer  
to obtain a more fluid prepolymer, it is preferred in this invention to utilize no solvent  
30 or diluent, as the removal of these ingredients require extra processing steps and  
possible environmental consequences from the use of these VOCs. Preferably, the  
50



polyurethane dispersions of the present invention are prepared in the substantial absence of an organic solvent.

Active hydrogen compounds are compounds having functional groups that contain at least one hydrogen atom bonded directly to an electronegative atom such as nitrogen, oxygen or sulfur. Various types of active hydrogen compounds, such as amines, alcohols, polyether polyols, polyester polyols, and mercaptans, for example, are known to those skilled in the art of preparing polyurethane polymers. Active hydrogen compounds suitable for use in the practice of the present invention can be polyols having molecular weights of less than about 10,000.

The aliphatic substituted hydroxy functional compound employed in the invention can consist of any compound possessing an aliphatic substituent of from 1 to 30 carbon atoms and one or more hydroxyl groups. Examples of such compounds include glycols such as glycerin, trimethylolpropane, or trimethylolethane which are partially esterified with a 1 to 30 carbon carboxylic acid, preferably a 5 to 22 carbon carboxylic acid, and more preferably a 10 to 15 carbon carboxylic acid. Examples of these compounds include the group consisting of glycerol monooleate, glycerol monobehenate, glycerol monotallate, glycerol monostearate, glycerol monopalmitate, trimethylolpropane monostearate, and mixtures thereof. Other types of compounds include polymeric versions of the aforementioned compounds, and copolymers of these compounds with other glycols, diols and acids or anhydrides. In addition, the aliphatic substituent may be attached to the hydroxyl portion of the compound via heteroatoms such as oxygen or nitrogen, such compounds include the N,N-bis(hydroxyalkyl) alkylamines, one example of which is N-stearyl diethanolamine. Branched chain hydroxy alkanes such as 1,2-dihydroxyoctadecane may also be used. Additionally sorbitan based esters such as the group consisting of sorbitan monostearate, sorbitan monooleate, sorbitan monolaurate, sorbitan monooleate, and mixtures thereof may also be used. Of these, the glycerol monoesters are preferred.

5 The aliphatic substituted hydroxy functional compound employed in the present invention can be used in a suprizingly low concentration to prepare polymers which are effective at repelling moisture. Preferably, the aliphatic substituted hydroxy functional  
10 compounds are present at a concentration of from 0.5 to 10 percent of the polymer weight of a polyurethane dispersion. More preferably, the aliphatic substituted hydroxy functional compounds are present at a concentration of from 1.0 to 4.5 percent of the  
15 polymer weight of a polyurethane dispersion and even more preferably, the aliphatic substituted hydroxy functional compounds are present at a concentration of from 1.5 to 2.5 percent of the polymer weight of a polyurethane dispersion.

20 Other types of aqueous polymeric dispersions can be used in combination with the polyurethane dispersions of the present invention. Suitable dispersions useful for blending with polyurethane dispersions of the present invention include: styrene-butadiene dispersions; styrene-butadiene-vinylidene chloride dispersions; styrene-alkyl  
25 acrylate dispersions; or acrylic dispersions; like compounds and mixtures thereof.

30 The present invention optionally includes a chain extender or a crosslinker. A chain extender is used herein to build the molecular weight of the polyurethane prepolymer by reaction of the chain extender with the isocyanate functionality in the  
35 polyurethane prepolymer, that is, chain extend the polyurethane prepolymer. A suitable chain extender or crosslinker is typically a low equivalent weight active hydrogen containing compound having about 2 or more active hydrogen groups per molecule. Chain extenders typically have 2 or more active hydrogen groups while crosslinkers  
40 have 3 or more active hydrogen groups. The active hydrogen groups can be hydroxyl, mercaptyl, or amino groups. An amine chain extender can be blocked, encapsulated, or otherwise rendered less reactive. Other materials, particularly water, can function to  
45 extend chain length and, therefore, can be chain extenders for purposes of the present invention.

50 Polyamines are preferred chain extenders. It is particularly preferred that the chain extender be selected from the group consisting of amine terminated polyethers

5 such as, for example, Jeffamine D-400 from Huntsman Chemical Company, amino  
ethyl piperazine, 2-methyl piperazine, 1,5-diamino-3-methyl-pentane, isophorone  
10 diamine, ethylene diamine, diethylene triamine, aminoethyl ethanolamine, triethylene  
tetraamine, triethylene pentaamine, ethanol amine, lysine in any of its stereoisomeric  
5 forms and salts thereof, hexane diamine, hydrazine and piperazine. In the practice of  
the present invention, the chain extender can be used as an aqueous solution.

15 While optional, in preparing a polyurethane polymer of the present invention  
use of a chain extender can be advantageous. Generally, a chain extender is employed  
10 in an amount sufficient to react with from zero (0) to 100 percent of the isocyanate  
20 functionality present in the prepolymer, based on one equivalent of isocyanate reacting  
with one equivalent of chain extender. It can be desirable to allow water to act as a  
chain extender and react with some or all of the isocyanate functionality present. A  
25 catalyst can optionally be used to promote the reaction between a chain extender and an  
15 isocyanate.

30 Catalysts are optional in the practice of the present invention. Catalysts suitable  
for use in the present invention include tertiary amines, and organometallic compounds,  
like compounds and mixtures thereof. For example, suitable catalysts include di-n-  
20 butyl tin bis(mercaptoacetic acid isooctyl ester), dimethyltin dilaurate, dibutyltin  
35 dilaurate, dibutyltin sulfide, stannous octoate, lead octoate, ferric acetylacetonate,  
bismuth carboxylates, triethylenediamine, N-methyl morpholine, like compounds and  
mixtures thereof. An amount of catalyst is advantageously employed such that a  
relatively rapid cure to a tack-free state can be obtained. If an organometallic catalyst is  
40 25 employed, such a cure can be obtained using from 0.01 to 0.5 parts per 100 parts of the  
polyurethane-forming composition, by weight. If a tertiary amine catalyst is employed,  
the catalyst preferably provides a suitable cure using from 0.01 to 3 parts of tertiary  
45 amine catalyst per 100 parts of the polyurethane-forming composition, by weight. Both  
an amine type catalyst and an organometallic catalyst can be employed in combination.

5 The present invention optionally includes a filler material. The filler material  
can include conventional fillers such as milled glass, calcium carbonate, aluminum  
trihydrate, talc, bentonite, antimony trioxide, kaolin, fly ash, or other known fillers. In  
10 the practice of the present invention, a suitable filler loading in a polyurethane  
5 dispersion can be from 100 to 1000 parts of filler per 100 parts of polyurethane.  
Preferably, filler can be loaded in an amount of at least about 200 pph, more preferably  
15 at least about 300 pph, most preferably at least about 400 pph.

The present invention optionally includes a filler wetting agent. A filler wetting  
10 agent generally can help make the filler and the polyurethane-forming composition  
20 compatible with one another. Useful wetting agents include phosphate salts such as  
sodium hexametaphosphate. A filler wetting agent can be included in a polyurethane-  
forming composition of the present invention at a concentration of at least about 0.5  
25 parts per 100 parts of filler, by weight.

15 The present invention optionally includes thickeners. Thickeners can be useful  
in the present invention to increase the viscosity of low viscosity polyurethane  
30 dispersions. Thickeners suitable for use in the practice of the present invention can be  
any thickener known in the art of preparing polyurethane dispersions. For example,  
20 suitable thickeners include ALCOGUM VEP-II\* (\*ALCOGUM™ VEP-II is a trade  
35 designation of Alco Chemical Corporation) and PARAGUM 231\* (\*PARAGUM 231  
is a trade designation of Para-Chem Southern, Inc.). Thickeners can be used in any  
amount necessary to obtain a dispersion of desired viscosity.

40 25 The present invention can include other optional components. For example, a  
polyurethane-forming composition of the present invention can include surfactants,  
blowing agents, frothing agents, fire retardant, pigments, antistatic agents, reinforcing  
45 fibers, antioxidants, preservatives, acid scavengers. Examples of suitable blowing  
agents include: gases and/or mixtures of gases such as, for example, air, carbon dioxide,  
30 nitrogen, argon, helium; liquids such as, for example, water, volatile halogenated

alkanes such as the various chlorfluoromethanes and chlorfluoroethanes; azo-blowing agents such as azobis(formamide).

Frothing agents are typically introduced by mechanical introduction of a gas into a liquid to form a froth (mechanical frothing). Mechanical frothing of a polyurethane polymer is a procedure known and practice by those skilled in the art of preparing polyurethane polymers. In preparing a frothed polyurethane foam, it is preferred to mix all components and then blend the gas into the mixture, using equipment such as an Oakes or Firestone foamer. In the preparation of a froth for a carpet backing, it is not necessary to obtain a froth that is stable. In a carpet backing production process, a frothed foam typically is spread on the back of a carpet using a spreading tool, which destroys the froth in the process.

Surfactants are optional, but can be desirable in the practice of the present invention. Surfactants useful herein can be cationic surfactants, anionic surfactants, or a non-ionic surfactants. Examples of anionic surfactants include sulfonates, carboxylates, and phosphates. Examples of cationic surfactants include quaternary amines. Examples of non-ionic surfactants include block copolymers containing ethylene oxide and silicone surfactants. Surfactants useful in the practice of the present invention can be either external surfactants or internal surfactants. External surfactants are surfactants which do not chemically react with the polymer to form a covalent bond during the preparation of the dispersion. Internal surfactants are surfactants which do become chemically reacted into the polymer during dispersion preparation. A surfactant can be included in a formulation of the present invention in an amount ranging from 0.01 to 20 parts per 100 parts by weight of polyurethane component. Preferably, the formulations of the present invention include polyurethane prepolymers which are not internal surfactants.

Generally, any method known to one skilled in the art of preparing polyurethane dispersions can be used in the practice of the present invention to prepare a moisture resistant polymer of the present invention. A moisture resistant polymer of the present

invention can be prepared from polyurethane dispersions that are storage-stable or polyurethane dispersions that are not storage-stable. A storage-stable polyurethane dispersion as described herein is any polyurethane dispersion having a mean particle size of less than about 5 microns. A polyurethane dispersion that is not storage-stable can have a mean particle size of greater than 5 microns. For example, a suitable dispersion can be prepared by mixing a polyurethane prepolymer with water and dispersing the prepolymer in the water using a commercial blender. Alternatively, a suitable dispersion can be prepared by feeding a prepolymer into a static mixing device along with water, and dispersing the water and prepolymer in the static mixer.

Continuous methods for preparing aqueous dispersions of polyurethane are known and can be used in the practice of the present invention. For example, U.S. Pat. Nos.: 4,857,565; 4,742,095; 4,879,322; 3,437,624; 5,037,864; 5,221,710; 4,237,264; and 4,092,286 all describe continuous processes useful for obtaining polyurethane dispersions. In addition, a polyurethane dispersion having a high internal phase ratio can be prepared by a continuous process as described in U.S. Pat. No. 5,539,021, incorporated herein by reference. In addition, it can be advantageous to combine a continuous process for preparing a prepolymer with a continuous feed dispersion process in order to maximize process efficiency as discussed in pending US Appl. Ser. No. 09/039978.

The polymers of the present invention can be applied to any substrate, but preferably the substrate is a textile. More preferably, the substrate is a carpet and the polymer is in the form of a moisture resistant backing. A carpet backing of the present invention can be prepared from a polyurethane dispersion of the present invention, described hereinabove, using either conventional or non-conventional methods in the art of preparing polyurethane-backed carpets. In preparing polyurethane-backed carpets of the present invention, a polyurethane-forming composition can be applied as a layer of preferably uniform thickness onto one surface of a carpet substrate. Polyurethane dispersions of the present invention can be applied as a precoat, laminate coat or as a foam coat. Polyurethane precoat, laminate coats, and foam coats can be prepared by methods known in the art. Precoat, laminate coats and foam coats prepared from dispersions are described in P. L. Fitzgerald, "Integral Latex Foam Carpet Cushioning",

5 J. Coat. Fab. 1977, Vol. 7 (pp.107 - 120), and in R. P. Brentin, "Latex Coating Systems for Carpet Backing", J. Coat. Fab. 1982, Vol. 12 (pp. 82 - 91), for example.

10 A polyurethane-forming composition can be applied to one surface of a carpet  
5 substrate before it cures to a tack-free state. Alternatively, a polyurethane dispersion containing completely reacted isocyanate functionality can be applied to a suitable  
15 substrate, thereby removing the need to cure the polymer. Typically the polyurethane-forming composition is applied to the surface that is attached to a primary backing but can be applied to a secondary backing such as mesh or fleece. The composition can be  
20 applied using equipment such as a doctor knife, air knife, or extruder to apply and gauge the layer. Alternatively, the composition may be formed into a layer on a moving belt or other suitable apparatus and dehydrated and/or partially cured, then married to the carpet substrate using equipment such as a double belt (also known as double band)  
25 laminator or a moving belt with an applied foam cushion. The amount of polyurethane-forming composition used can vary widely, from 5 to 500 ounces per square yard, depending on the characteristics of the textile. After the layer is applied and gauged, water is removed from the dispersion and the layer can be cured using heat from any  
30 suitable heat source such as an infrared oven, a convection oven, or heating plates.

35 In the practice of the present invention, any of the steps used in preparing a polyurethane carpet backing can be carried out in a continuous manner. For example, in a first step the prepolymer can be prepared from a suitable active hydrogen containing compound in a continuous manner; the prepolymer can be fed, as it is  
40 obtained in the first step, into a mixing device with water to obtain an aqueous  
25 dispersion; the aqueous dispersion can be applied to a carpet substrate in a continuous manner to obtain a polyurethane backed carpet.

45 The following example is provided to illustrate the present invention. The example is not intended to limit the scope of the present invention and should not be so  
30 interpreted.

Example 1

A prepolymer, hereinafter Prepolymer A, is prepared as follows:

195.7 parts (0.1957 eq.) of VORANOL 5287\*, a 12.5 percent ethylene oxide capped polypropylene oxide diol with an equivalent weight of 1000 g/eq; 93.02 parts (0.7442 eq.) of ISONATE 25OP\*, a mixture of 25 percent 2,4'-MDI and 75 percent 4,4'-MDI; 5.28 parts (0.02966 eq.) of EMEREST 2421\* glycerol monooleate and 6.0 parts (6.316 meq) of polyethylene glycol monol (MPEG) having a molecular weight of 950 are mixed with heating to 70°C in a glass vessel for about 15 hours. The resultant prepolymer has a percent NCO of 6.88, an isocyanate equivalent weight of 610, and a viscosity of 6040 cps @ 25 C. (EMEREST 242 is a trade designation of the Henkel Corp; VORANOL 5287 and ISONATE 25OP is a trade designation of The Dow Chemical Company).

A polyurethane dispersion is prepared as follows:

75.58 parts of Prepolymer A; 9.9 part of a DESULF DBS-25T\*, a 25 percent aqueous solution of a triethanolamine salt of dodecyl benzene sulfonic acid; and 20.08 parts of water are mixed at room temperature and then stirred at 3000 rpm in a glass flask. 44.4 parts of a 10 percent aqueous piperazine solution is added to the mixture, and stirring is continued for 1 minute at 3000 rpm. The resulting mixture is then stirred overnight with a stir bar and is filtered through a paint filter to yield a low viscosity, 55 percent solids polyurethane dispersion with a mean particle size of 0.24 microns. (\*DESULF DBS-25T is a trade designation of DeForest Chemical Co.)

A carpet backed with the polyurethane dispersion is prepared as follows:

The dispersion is compounded by admixing 178.6 parts of the dispersion (100 parts solids) and 200 parts calcium carbonate filler. Then, 3.0 parts of PARAGUM 241\* thickener is admixed. The compound is applied to the back of a nylon level loop style carpet with a greige weight of 23 oz/yd<sup>2</sup> (0.8 kg/m<sup>2</sup>) at a coating weight of 38.5 oz/yd<sup>2</sup> (1.3 kg/m<sup>2</sup>). A polypropylene scrim, 3.3 oz/yd<sup>2</sup> (0.11 kg/m<sup>2</sup>), is applied as a secondary backing. The carpet is dried at 132°C for 12 minutes, then allowed to equilibrate



overnight before testing. (\*PARAGUM 241 is a trade designation of Para-Chem Southern, Inc.)

The carpet is tested as follows:

The carpet of Example 1 has a tuftlock of 17.4 pounds (7.9 kg), and a rewet tuftlock of 11.2 pounds (5.1 kg). Tuftbind values are obtained according to ASTM D1335. The carpet of Example 1 has a dry delamination of 10.1 pounds/in. (1.8 kg/cm) and a re-wet delamination of 5.0 pounds/in 0.89 kg/cm). The delamination is the strength required to remove the secondary polypropylene scrim from the fabricated carpet. It is determined by cutting a 3 inch by 9 inch (7.6 cm x 22.9 cm) strip of carpet, and peeling the secondary scrim from the main portion of the carpet while measuring the force required. The rewet delamination is determined in the same manner, except that the carpet specimen is soaked for one minute in water, and blotted dry prior to testing. The carpet has a hand punch of 17.7 pounds (8.0 kg). The hand punch is measured as the force required to push a 9 inch by 9 inch (22.9cm x 22.9 cm) piece of carpet 0.5 inches (1.27 cm) into a 5.5 inch (14 cm) inner diameter cylinder at a rate of 12.0 inches (30.5 cm) per minute, using a 2.25 inch (5.7 cm) outer diameter solid cylinder attached to a load cell. The carpet passes a water resistance test known as the British spill test in which 100 ml of a solution of methylene blue dye in water is poured from a height of 1 meter onto a 12x12 inch (30.5 cm x 30.5 cm) piece of carpet and allowed to stand for 24 hours. The sample is inscribed with a razor knife to reveal the interior. A pass rating is given if no blue dye is found to have penetrated into or through the backing.

#### Example 2

A prepolymer and dispersion are prepared as in Example 1. The procedure of Example 1 is used to compound the dispersion, except that 100 parts of calcium carbonate, 100 parts of Gamma Sperse CS-11\*, and 0.6 parts of PARAGUM 241 are used to compound the dispersion. The compound is applied to the back of a carpet at a coat weight of 37.1 oz/yd<sup>2</sup> (1.26 kg/m<sup>2</sup>) and the resulting carpet gave the following test results:

Hand (lb.) 13.8 (6.3 kg)

Tuftlock (lb.) 19.8 (9.0 kg)

Rewet Tuftlock (lb.) 13.3 (6.0 kg)

British Spill Test pass

- (\* Gamma Sperse CS-11 is a calcium carbonate which has been treated with ammonium stearate to provide improved hydrophobic properties and is a trade designation of Georgia Marble Co.)

### Comparative Example 3

- Prepolymer B is prepared as follows:

190.85 parts (0.1908 eq.) of VORANOL 5287; 99.25 parts (0.794 eq.) of ISONATE 25OP\*, a mixture of 25 percent 2,4'-MDI and 75 percent 4,4'-MDI; 3.9 parts (0.07358 eq.) of diethylene glycol; and 6.0 parts (6.316 meq) of polyethylene glycol monol (MPEG) having a molecular weight of 950 are mixed with heating to 70°C in a glass vessel for about 15 hours. The prepolymer has a percent NCO of about 7.3, an isocyanate equivalent weight of about 575, and a viscosity of about 7000 cps @ 25 C. (\*ISONATE 25OP is a trade designation of The Dow Chemical Company).

A polyurethane dispersion is prepared as follows:

- 75.5 parts of Prepolymer B; 9.9 parts of a 25 percent aqueous solution of the triethanolamine salt of dodecyl benzene sulfonic acid; and 19.3 parts of water are mixed at room temperature and then stirred at 3000 rpm in a glass flask. 45.3 parts of a 10 percent aqueous piperazine solution is added to the mixture, and stirring is continued for 1 minute at 3000 rpm. The resulting mixture is stirred overnight with a stir bar and filtered through a paint filter to yield a low viscosity, 55 percent solids polyurethane dispersion with a mean particle size of 0.3 microns.

A Carpet backed with the polyurethane dispersion is prepared as follows:

5 The dispersion is compounded by admixing 178.6 parts dispersion (100 parts solids)  
with 200 parts calcium carbonate filler. 4.1 parts of PARAGUM 241 is then admixed.  
10 The compound is applied to the back of a nylon level loop style carpet with a greige  
weight of 23 oz/yd<sup>2</sup> (0.8 kg/m<sup>2</sup>) at a coating weight of 38.5 oz/yd<sup>2</sup> (1.3 kg/m<sup>2</sup>). A  
5 polypropylene scrim, 3.3 oz/yd<sup>2</sup> (0.11 kg/m<sup>2</sup>), is applied as a secondary backing. The  
carpet is dried at 132°C for 12 minutes, then allowed to equilibrate overnight before  
15 testing.

The carpet is tested as follows:

20 10 The carpet of Comparative Example 3 is tested substantially identically to the carpet of  
Example 1. It has a tuftlock of 18.5 pounds (8.4 kg), and a rewet tuftlock of 8.9 pounds  
(4.0 kg). The carpet of Comparative Example 3 has a dry delamination of 10.1  
25 pounds/in. (1.8 kg/cm) and a rewet delamination of 5.0 pounds/in. (0.89 kg/cm). The  
carpet of Comparative Example 3 has a hand punch of 14.7 pounds (6.7 kg). The  
15 carpet failed the British spill test.

#### 30 Comparative Example 4

35 A prepolymer and dispersion are prepared as in Comparative Example 3. The  
procedure of Comparative Example 3 is used to compound the dispersion, except that  
20 100 parts of calcium carbonate, 100 parts of GAMMA SPERSE CS-11, and 0.98 parts  
of PARAGUM 241 are used to compound the dispersion. The compound is applied to  
40 the back of a carpet at a coat weight of 38.5 (1.3 kg/m<sup>2</sup>)oz/yd<sup>2</sup>, and the resulting carpet  
gave the following test results:

45	25	Hand (lb.)	11.8 (5.4 kg)
		Tuftlock (lb.)	18.9 (8.6 kg)
		Rewet Tuftlock (lb.)	12.4 (5.6 kg)
50		British Spill Test	fail

## Claims

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## CLAIMS

What is claimed is:

1. An aqueous polyurethane dispersion comprising an isocyanate terminated prepolymer prepared from a formulation including a polyisocyanate and a polyol mixture, wherein the polyol mixture includes at least one aliphatic mono, di or polyhydroxy compound which has an aliphatic side chain substituent which contains from 5 to 30 carbon atoms and wherein the aliphatic mono, di or polyhydroxy compound which has an aliphatic side chain substituent is present at a concentration of from 0.5 to 10 weight percent of the polymer.
2. The aqueous polyurethane dispersion of Claim 1 wherein the polyisocyanate is MDI.
3. The aqueous polyurethane dispersion of Claim 1 wherein the aliphatic mono, di or polyhydroxy compound which has an aliphatic side chain substituent which contains from 5 to 30 carbon atoms is a glycerol monoester.
4. The aqueous polyurethane dispersion of Claim 1 wherein the dispersion is prepared with an external surfactant.
5. The aqueous polyurethane dispersion of Claim 1 wherein the polyol mixture includes a polyether polyol.
6. The aqueous polyurethane dispersion of Claim 1 wherein the dispersion is prepared in the substantial absence of an organic solvent.
7. The aqueous polyurethane dispersion of Claim 1 wherein the dispersion is compounded with a filler.

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8. The aqueous polyurethane dispersion of Claim 11 wherein the filler is calcium carbonate.

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9. Use of the aqueous polyurethane dispersion of Claim 1 to prepare a moisture resistant textile.

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10. The use of Claim 9 wherein the textile is a carpet.

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## INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/US 99/28804

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08G18/66 C08G18/32

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 096 127 A (SCHURMANN HORST ET AL) 20 June 1978 (1978-06-20) column 2, line 64 - column 3, line 68; claims 1,5,6	1-3
X	US 5 417 723 A (TRAEUBEL HARRO ET AL) 23 May 1995 (1995-05-23) claim 1; examples	1,3
A	US 5 712 342 A (KIM YANG BAE ET AL) 27 January 1998 (1998-01-27) claims 1,13,15	1,3,7,9
A	WO 98 12273 A (PPG INDUSTRIES INC) 26 March 1998 (1998-03-26) page 7, line 10 - line 19; claims 1,4,5	1-4,9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

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- \*P\* document published prior to the international filing date but later than the priority date claimed

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- \*8\* document member of the same patent family

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/28804

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4096127 A	20-06-1978	DE 2457972 A	16-06-1976
		AR 208936 A	15-03-1977
		AT 356510 B	12-05-1980
		AT 611077 A	15-09-1979
		AT 343915 B	26-06-1978
		AT 911175 A	15-10-1977
		AU 8681075 A	26-05-1977
		BE 836210 A	01-04-1976
		BR 7508038 A	24-08-1976
		CA 1068440 A	18-12-1979
		CH 622535 A	15-04-1981
		CS 198254 B	30-05-1980
		DD 128378 A	16-11-1977
		ES 442993 A	01-07-1977
		FI 753272 A, B,	08-06-1976
		FR 2293449 A	02-07-1976
		GB 1516340 A	05-07-1978
		HU 173146 B	28-03-1979
		IE 42099 B	04-06-1980
		IL 48499 A	29-09-1978
		IT 1052461 B	20-06-1981
		JP 1048824 C	28-05-1981
		JP 51088598 A	03-08-1976
		JP 55041607 B	25-10-1980
		NL 7514248 A, B,	09-06-1976
		NO 754055 A, B,	09-06-1976
		SE 425397 B	27-09-1982
		SE 7513727 A	08-06-1976
		YU 308275 A	27-04-1983
		ZA 7507197 A	27-10-1976
US 5417723 A	23-05-1995	DE 4421292 A	21-12-1995
US 5712342 A	27-01-1998	KR 167002 B	20-03-1999
WO 9812273 A	26-03-1998	AU 4583197 A	14-04-1998